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Letter

NiPt hollow nanocatalyst: Green synthesis, size control and electrocatalysis

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Abstract

Nearly monodispersed hollow nanospheres of bimetallic NiPt have been synthesized by a one-pot wet chemical method at room temperature with a precursor Ni nanocompound as a sacrificial template. The size control is carried out via the sacrificial template, from about 35 nm to nearly 100 nm in diameter. The shell thickness of the NiPt hollow sphere reaches down to as thin as 2–3 nm slightly larger than a single layer of alloyed NiPt nanocrystallites. The product with the citric acid as surfactant exhibits enhanced oxygen reduction activities compared to a commercial Pt/C catalyst and the hollow nanospheres coated with PVP. It has potential applications in fuel cells, biotechnology and environmental chemistry with the facile synthesis, low cost and excellent electrocatalytic activity.

Keywords: Bimetallic nanoparticles; NiPt alloy; Hollow structure; Electrocatalysis

1. Introduction

In the past few years, the synthesis of Pt-based bimetallic catalyst has received much attention due to its wide range of applications such as direct methanol fuel cells (DMFCs) [1–3]. Because of the high cost, a lot of efforts have been devoted to reduce the utilization of Pt, without sacrifice of or even improving its functionality. The research has focused on the manipulation of the size, morphology, composition and structure. Recently, different morphologies have been synthesized [4–10]. Among them the hollow structure might be a promising one due to its unique characteristics such as low density, reduced cost, and high surface area [11–15].

In this study, nearly monodispersed hollow nanospheres of bimetallic NiPt with very thin shell, 2–3 nm, were synthesized. The synthesis was carried out by a one-pot wet chemical method at room temperature with a precursor Ni nanocompound as a sacrificial template. The size and composition has been tuned by adjusting the reaction time and introducing suitable amounts of precursory molecules. In addition, the catalytic properties were also reported, showing better performance and longer relaxation in catalytic activity in comparison with the commercial Pt/C catalyst.

2. Experimental

$C_6H_8O_7$ (citric acid), $NiCl_2 \cdot 6H_2O$ (nickel chloride hexahydrate), $NaBH_4$ (sodium borohydride), and $H_2PtCl_6 \cdot 6H_2O$ (chloroplatinic acid hexahydrate) were purchased from Chinese reagent companies. All reagents were analytic grade and used as received.

In a typical synthesis, 8 mg $C_6H_8O_7$ was dissolved in 100 ml DI water, then 0.2 ml $NiCl_2$ aqueous solution (0.5 g in 10 ml DI water) was added into the $C_6H_8O_7$ aqueous solution. The mixed solution was sonicated for 15 min and

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then protected in the argon. Freshly prepared 13 mg $NaBH_4$ powder was then added quickly with vigorous stirring. Meanwhile the intermediate products containing Ni and B were produced. Immediately after the solution turning black, H_2PtCl_6 (20 ml, 1 mM) was added dropwise. After 120 min, the products were collected by centrifugation and washed several times with ethanol.

The morphologies and chemical compositions of the as-synthesized products were characterized by X-ray diffractometry (XRD, X'Pert Pro MPD system, Cu Ka, λ=0.154 nm), scanning electron microscopy (SEM, Hitachi S-4800) with an energy dispersive X-ray spectroscope (EDS), and transmission electron microscopy (TEM, JEOL 2100 F at 200 kV). SEM specimens were prepared by dropping the solution of powder in ethanol over the Si substrate, whereas the TEM specimen was prepared by dispersing the powder in ethanol with ultrasonic treatment and dropping on a Cu-grid coated, porous carbon film.

To prepare the working electrode, Pt catalyst (2.7 mg $Ni_{0.5}Pt_{0.5}$, 2.3 mg $Ni_{0.3}Pt_{0.7}$ and 5.2 mg Pt/C 40% commercial catalyst) was dispersed ultrasonically in 2 mL of absolute ethyl alcohol, and 4 μL of the suspension was pipetted onto a glassy carbon substrate (φ 6 mm). Then 3 μL Nafion was dropped onto the substrate. The coated electrode was dried in air. The loading of platinum was about 15 μg cm^{-2}. Electrochemical experiments were carried out in a standard three-electrode cell at room temperature (about 25 °C). The working electrode was a Pt foil and the reference electrode was a saturated calomel electrode (SCE). Electrode potential was controlled by a CHI 660C potentiostat/galvanostat.

3. Results and discussion

3.1. Characterization

The morphologies were observed using TEM. Fig. 1(a) shows an image of monodispersed NiPt nanospheres with high uniformity of shell thickness on a large scale. The average diameter is determined ~35 nm. Particularly, the shell is extremely thin, about 2–3 nm as shown in Fig. 1(b) by a typical high-resolution TEM image for a part of a nanosphere. The lattice fringes with a d spacing of 0.231 nm are determined, corresponding to the (1 1 1) interplanar distance of face-centered cubic (fcc) crystalline Pt. The nanospheres are formed with well-crystallized but randomly orientated nanoparticles of a few nanometres. Amorphous regions have also been observed in the boundary area between the nanocrystallites.

Fig. 1(c) is EDS spectrum of the sample acquired by SEM, showing mainly Ni, Pt and Si characteristic peaks. Knowing that Si originates from the silicon substrate, we conclude that the as-synthesized samples contain only two elements, nickel and platinum with an atomic ratio of ~1:1. The powder XRD pattern of as-synthesized material is recorded in Fig. 1(d). It exhibits a typical pattern similar to that of a pure Pt phase

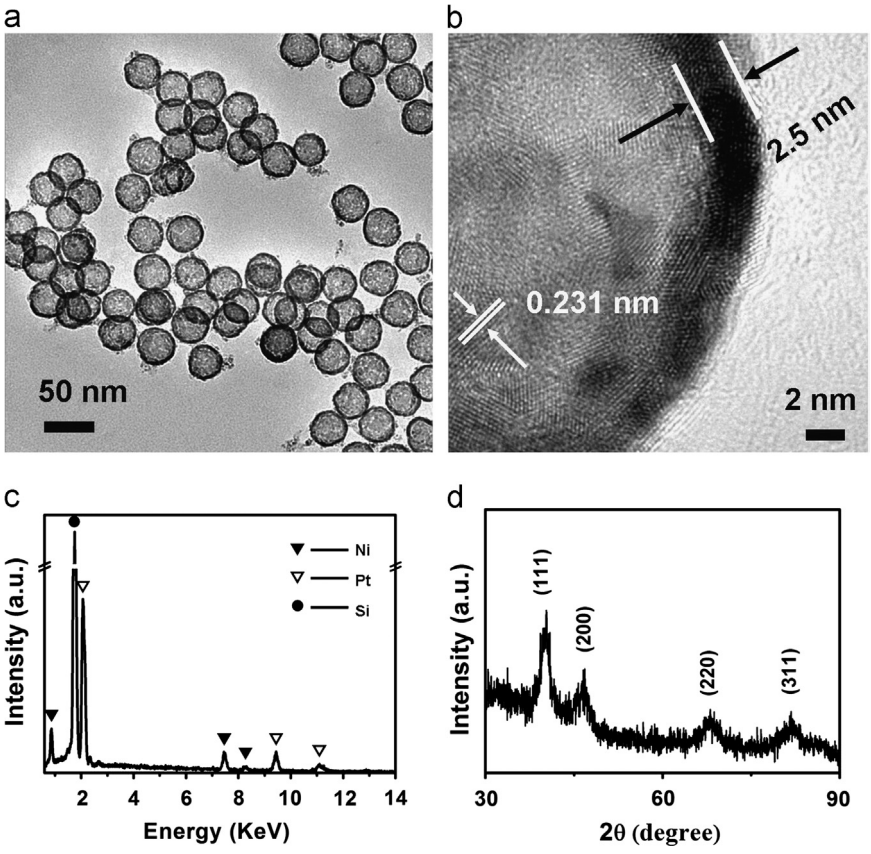

Fig. 1. (a) A TEM image of NiPt nanospheres of about 35 nm in diameter; (b) a typical high-resolution TEM image for a part of nanosphere; (c) EDS analysis for the same product and (d) XRD pattern, indexed to Pt (JCPDS no. 87-0647).

without showing that of a Ni phase. This would be the first sign suggesting that nanocrystallites of PtNi alloy might have formed.

3.2. Control of size and composition

Monodispersed NiPt nanospheres with different sizes ranging from 35 to more than 100 nm have been synthesized. TEM images for three typical nanospheres of 105, 85 and 35 nm are shown in Fig. 2(a–c), respectively. Normally, the size control is realized mainly by adjusting the concentration of the reactants and/or the surfactant, as reported in the literature[16] and confirmed in the present work. However, the size control has been carried out also by controlling the reaction time to manipulate the size of the precursor Ni nanoparticles, as shown in Fig. 2(d)–(f). As time goes by, the size of the Ni compound particles is reduced uniformly by stirring vigorously. The reason for the decrease of the particles size could be the corroding action made by the chlorine ions in the solution. Thus we can control the reaction time before adding chloroplatinic acid to obtain NiPt hollow spheres with different sizes. In addition the compositions of Pt can be controlled by adjusting the concentration of Pt^{4+} precursor solution. As shown in Fig. 2(a), Pt-rich particles can be produced using a high concentration Pt^{4+} precursor solution. With decreasing of the Pt^{4+} concentration, the Pt composition of the final products will be reduced, as shown in Fig. 2(b) and (c).

3.3. Catalysis

Three samples were tested in the catalytic experiment, namely, 35 nm NiPt hollow nanoparticles synthesized with citric acid as surfactant using the above method, NiPt hollow

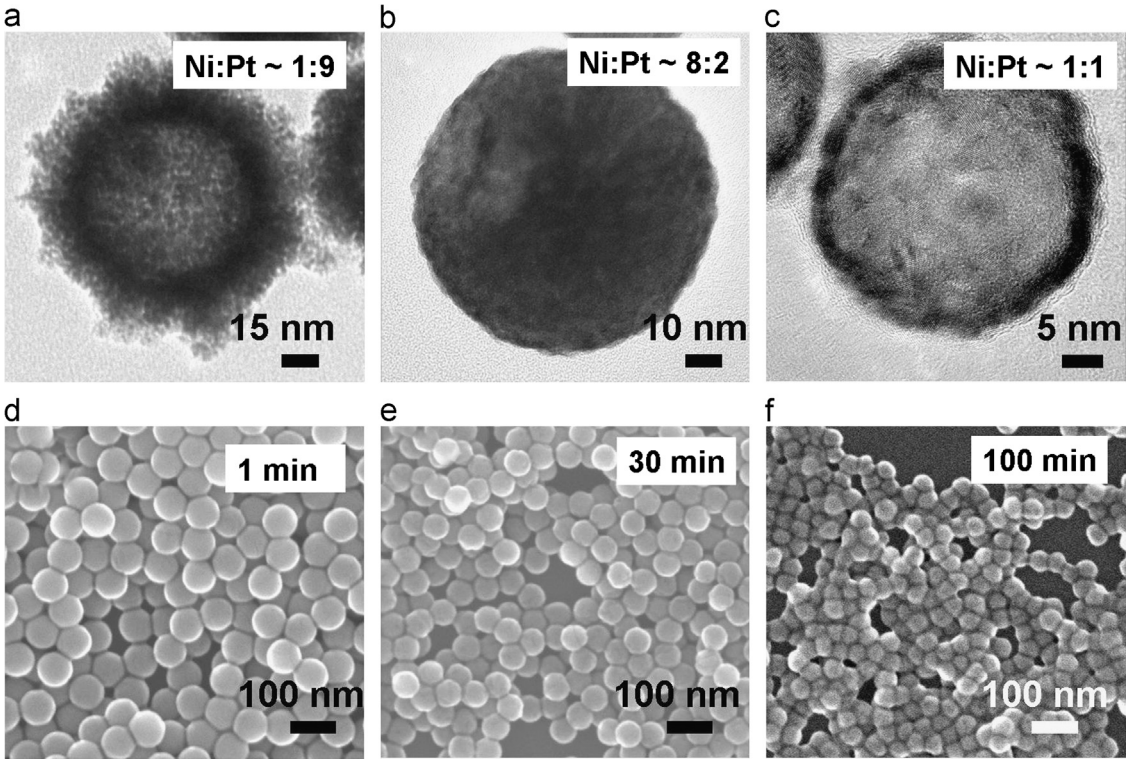

Fig. 2. Control of size and composition. (a)–(c) NiPt nanospheres with a different atomic ratio of Ni and Pt. (d)–(f) Ni template with different sizes.

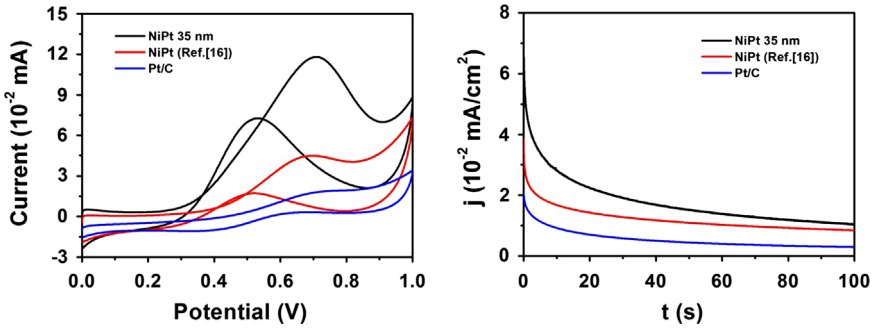

Fig. 3. (a) Cyclic voltammograms and (b) chronoamperometry results of methanol oxidation at 0.65 V on 35 nm NiPt hollow spheres (black), NiPt hollow spheres synthetized according to Ref. [16] (red) and commercial Pt/C (blue) in 0.5 M sulfuric acid (H_2SO_4) solution containing 0.5 M methanol (CH_3OH).

spheres synthesized with PVP (Polyvinyl Pyrrolidone) as the surfactant according to Ref. [16] and commercial Pt/C. The electrocatalytic activity of these three samples in the oxidation of methanol was tested in the 0.5 M H_2SO_4 and 0.5 M CH_3OH between 0 V and 1.0 V at the sweep rate of 50 mV s^{-1}. As shown in Fig. 3(a), during the positive scan, the current increases until a peak is seen at 0.69 V, which is attributed to electro-oxidation of methanol. When the potential scan is reversed, a peak at 0.52 V occurs, which is due to the reactivation of Pt-oxides. The 35 nm NiPt hollow nanoparticles showed the highest forward current density (11.9 mA cm^{-2}), which is 2.6 and 6.9 times higher than NiPt hollow spheres (Ref. [16]) and commercial Pt/C, respectively.

The electrocatalytic activity and stability of these three samples were further compared by using chronoamperometry test at 0.65 V. The oxidation current has been normalized to the same Pt weight so that the current density can be directly used to compare the catalytic activity of different samples. The oxidation current density on the 35 nm hollow NiPt nanosphere is much higher than NiPt hollow spheres (Ref. [16]) and Pt/C catalyst. This result combined with the cyclic voltammetry measurements further confirms that the electrocatalytic activity and stability of 35 nm hollow NiPt catalysts are higher than that of hollow NiPt catalysts (Ref. [16]) and Pt/C catalysts. The much enhanced catalytic activity for the methanol oxidation may be attributed to the increasing specific surface, due to the additional active sites provided by the inner surface of the NiPt hollow nanospheres [17–21].

4. Conclusions

In summary, nearly monodispersed hollow nanospheres of bimetallic NiPt were synthesized by a one-pot wet chemical method at room temperature. The nanospheres with different ratios of Ni and Pt constituents have been obtained. The size of the Ni sacrificial template might have played a role, in addition to the concentration of the reactants and surfactant, in the size control of the NiPt nanospheres. The synthesized hollow NiPt nanospheres exhibited considerably enhanced oxygen reduction activities compared to commercial Pt/C catalyst and hollow NiPt catalysts coated with PVP.

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